NASA Technical Memorandum 87155

Evaluation Parameters for the Alkaline Fuel Cell Oxygen Electrode

(NASA-TM-87155) EVALUATION PARAMETERS FOR THE ALKALINE FUEL CELL OXYGEN ELECTRODE (NASA) 13 p HC A02/MF A01 CSCL 07D

N86-12268

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G3/25 04841

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NOV 1985
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November 1985

NASA

EVALUATION PARAMETERS FOR THE ALKALINE FUEL CELL OXYGEN ELECTRODE

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SUMMARY

Studies were made of Pt- and Au-catalyzed porous electrodes, designed for the cathode of the alkaline H_2/O_2 fuel cell, employing cyclic voltammetry and the floating half-cell method. The purpose was to obtain parameters from the cyclic voltammograms which could predict performance in the fuel cell. It was found that a satisfactory relationship between these two types of measurement could not be established; however, useful observations were made of relative performance of several types of carbon used as "supports" for noble metal catalysts and of some Au catalysts. The best half-cell performance with H_2/O_2 in a 35 percent KOH electrolyte at 80 °C was given by unsupported fine particle Au on Teflon; this electrode, developed by UTC (now IFC), is used in the Orbiter fuel cell.

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INTRODUCTION

In view of the need for reliable long life alkaline fuel cells, especially for space power applications, tests are much desired which can predict performance of fuel cell electrodes. In this work the electrode studied was the cathode of the alkaline oxygen fuel cell. The basic approaches for obtaining predictive parameters could be based on the techniques of cyclic voltammetry, polarization, and current interruption. In the present study the first two techniques were employed to obtain information about the electrodes. The electrodes investigated were specially fabricated porous carbon electrodes with various amounts of dispersed platinum or gold as active catalysts. Unsupported gold platinum alloy was also examined. In alkaline fuel cells the carbon plays an important role in electron transfer reactions. The most important electrochemical function of C in alkaline electrolyte is the production of the perhydroxide ion, HO_2^-, which is then (ref. 1) chemically decomposed by the incorporated metal catalyst to oxygen and OH^-. Corrosion of carbon is a problem; the corrosion is most severe at high anodic potentials (ref. 2) but it occurs in the alkaline fuel cell at its more anodic potentials, e.g. open circuit voltages. The stability of carbon against such corrosion can be improved by various treatments of carbon. In this study carbons were employed that had been treated in different ways.

In cyclic voltammetric experiments current-voltage measurements are made between the regions of hydrogen evolution and oxygen evolution on test electrodes. The regions of interest were the hydrogen adsorption region, the integrated value of which is a measure of available platinum for the catalysis

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(ref. 3), and the double-layer region, whose width, (dl), is a measure of total available surface area (including both carbon and platinum); this width represents the total capacitance which is given by the area between the electrocatalyst and electrolyte. The floating half-cell (ref. 4) was employed for obtaining the current-voltage data regarded as closely indicative of fuel cell performance.

In these studies, correlation which might predict fuel cell performance was sought between the cyclic voltammetric data and the polarization data. During the course of the work the morphology of some Au materials became a matter of interest for which electron microscopy and diffraction were employed.

EXPERIMENTAL

Electrodes

The electrodes studied are given in table I. The five Pt/C and the one Au/C electrodes were fabricated by Giner Inc., as 5x7 in. sheets on Ni screen, in the form of practical fuel cell electrodes. The second gold electrode, specimen 7, is a piece of IFC (formerly UTC) alkaline fuel cell cathode. Only this last electrode is an actual fuel cell cathode, although the others were fabricated exactly as practical electrodes would be made for this application.

Apparatus

For both cyclic voltammetric and polarization measurements a PAR Model 173 Potentiostat/Galvanostat was used. The ramp voltages were generated by an ECO Model 566 Function Generator. An X-Y recorder was used for the display of the current-voltage curves. The IR corrections for the polarization curves were obtained with the Electrosynthesis Corp. current interrupter. The reference electrode was a dynamic hydrogen electrode (DHE).

The cyclic voltammetric curves were obtained in 1 N H_2SO_4 at 25 °C. For these measurements the electrodes were first wetted with 20 percent isopropanol-water, rinsed, and preconditioned by polarizing at +1.45 V versus the DHE for 1 min and at 0.0 V for 1 min. This treatment was repeated to remove adsorbed organic impurities from the catalyst surface. The electrodes were then subjected to cyclic sweeps between +0.035 and +1.35 V at 5 mV/s. The voltammograms were recorded when they were steady and reproducible.

Polarization data were obtained galvanostatically in a floating half-cell (ref. 4). The electrolyte, 35 percent KOH at 80 °C, was used also in a presaturator through which bottled oxygen flowed en route to the half-cell. E-I curves were recorded at current densities from 0 to 200 mA/cm^2. Voltages at 100 and 200 mA/cm^2 were read and corrected for IR drop.

The Au-10% Pt electrode material was examined by electron microscopy and electron diffraction with the expectation of (1) observing the crystal morphology of the ~150 Å particles, and (2) obtaining diffraction from small regions at their edges.

RESULTS

In the cyclic voltammetric measurements (fig. 1) the parameters studied were:

(1) H-adsorption area as a measure of effective platinum catalyst area, using the accepted factor of 210 $\mu C/cm^2$ for platinum (ref. 3)
(2) Width of the double layer region, dl, as a relative measure of the effective capacitance of the electrode
(3) Resolution of the H-adsorption peaks (ref. 7) for possible grading of the Pt. It soon appeared that only an evaluation as "good" or "poor" might be warranted, but even this terminology was not useful.

Table II summarizes the data obtained from cyclic voltammetry in 1 N sulfuric acid at 25 °C and from half-cell polarization measurements using oxygen at 80 °C in 35 percent KOH. The half-cell voltages were corrected for ohmic drop. Samples 1, 5, and 6 were also corrected for catalyst loading so that the observed currents could be compared for loadings normalized to 1 mg/cm^2. This was done graphically by reading the voltage from the polarization curve at current values twice those of the experimentally observed values. Specimens from the same sample were within 10 percent of each other with regard to polarization and cyclic voltammetric area. The areas reported here were measured about 9 months after the receipt of the electrodes; some of the samples of the same material had been studied within 2 months of receipt and they indicated higher areas by about 30 percent.

Figure 1 is presented as representative of the cyclic voltammograms (CV) obtained with Pt/C electrodes in H_2SO_4. Table II shows no significant connection between CV features and the half-cell performance, so the individual CV have not been reproduced. Figure 2 consists of the I-E runs for samples 5 to 7. Since 7 is the 20 mg/cm^2 Au-10% Pt IFC electrode, and both 5 and 6 are 0.5 mg/cm^2 Pt-on-carbon electrodes, no corrections for loading were made for this figure. However the IR corrections at 100 and 200 mA/cm^2 are designated by arrows. Sample 5 has been taken to represent the Pt/C electrodes, particularly because of its low polarization.

Electron microscopy of the Au-10% Pt powder which is used to make the IFC electrode disclosed continuous irregular clumps of particles. The Pt was not distinguishable from the Au, although some of the Pt is said to be only partially alloyed (ref. 6). The particles were impossible to separate which resulted in their morphology being visible only at the edges of clumps where hints of only hexagonal forms could be seen (ref. 7). Electron diffraction with beams as small as 1.5 μ yielded random spots, indicating the presence of small crystallites, appreciably smaller than the particles, in random orientation.

DISCUSSION

That catalyst surface area which is determined from hydrogen adsorption in acid medium might be expected to correlate with any catalytic process which depends on the area of available catalytic surfaces. There is indeed observed here a weak correlation with the polarization results, more so at 100 mA/cm^2 than at 200 mA/cm^2. At the higher current densities, factors other than catalyst area appear to predominate, such as blockages in the pore structure of the electrode inhibiting mass transport in the solution.

In principle, the width of the double-layer region is related to the combined surface areas of the Pt catalyst and the carbon support. Because of the porous nature of the supporting high surface area carbon, one can safely assume that the width, dl, is essentially determined by the carbon porosity. Further, and differing from Pt where hydrogen adsorption is the dominant factor, neutral organic molecules tend to adsorb on C in the dl region, thus weakening correlation between dl and current density. The data, table II, show no correlation between dl measurements and polarization.

The effect of heating as a pretreatment is seen in table II for electrodes 3 and 4. They show about the same polarization, medial in this series, which suggests a similar effect due to heating even at such disparate temperatures. The 2700 °C heating undoubtedly graphitized the C fully, but the 1050 °C pretreatment should do no more to the C than desorb the impurities. However, 1050 °C is reported to have some effect on the Pt, possibly even forming some Pt carbides (ref. 5). A more extensive study would be required to identify these individual effects.

The E-I charts from the 80 °C half-cell runs are reproduced in figure 2 for specimens 5 to 7. Comparing polarization between 100 and 200 mA/cm^2, specimens 5 and 6 are directly comparable in regard to their catalyst loading, but certain inferences may be drawn from comparing them with specimen 7 despite its 20 mg/cm^2 loading. These three electrodes show less polarization than the other four. It may be inferred that the structures of electrodes 5, 6, and 7 show less mass-transport polarization; the four others do have voluminous carbon in the active part of the structure. In order to further enable the comparisons among all the C-supported catalysts (1 to 6), the voltages in table II were corrected also for loading. This correction is based on the assumption that the current is proportional to loading of the catalyst (ref. 8), and on the facts that the reduction of oxygen to hydrogen peroxide on carbon is rapid and reversible, and that the current is limited by the catalytic reaction rate (ref. 1).

Despite the factor of 20 or 40 between the loading of specimen 7 and the others, certain speculations may be made from the half-cell data obtained with specimen 7. These are in agreement with the IFC performance data from an operational fuel cell assembly, i.e., the polarization is very low. The original half-cell chart (not reproduced here) shows continued low polarization up to 1 A/cm^2. Electrode 6 had been designed to examine the effect of dispersing fine Au particles on C, and was fabricated analogously to Pt/C structures, the interest stemming from possibilities of reducing the quantity of gold catalyst required and providing high surface area and high dispersion of the gold.

It is observed that specimen 7 has some inherent superiority over any of the others. The low polarization may be due to the absence of a second phase, namely carbon, thus minimizing mass-transport polarization. Specimen 5, while it has C also, does not have the loose, high area, carbon structure of electrodes 1 to 4 and 6, and it also shows low polarization. Implicit in the performance of unsupported gold is the ability of gold alone to perform the entire reduction/catalysis with at least the efficiency of Pt/C. Electronic conduction from the surface of the gold to the mounting screen is effected by the tightly clumped gold (aided by heavy loading) and also by microcracks in the

Teflon embedded in the screen. It has been reported that when the electrode is heated to 500 °F in fabrication, these cracks appear, allowing the gold to make contact to the collector screen.

Separate consideration is warranted in the matter of activity of Au. Classically Au has been considered a poor catalyst for oxygen reduction (ref. 9). The performance since 1977 by the oxygen catalytic electrode in Orbiter missions seems to have gone unnoticed in the literature, yet published IFC (then, UTC) data show test stand runs with 6-cell stacks at 62 °C in 35 percent KOH for 18 000 hr (ref. 15).

How does one reconcile these two apparently contradictory views of Au as an oxygen catalyst? These suggestions are herewith made:

(1) The (100) plane of single crystals of Au has been shown to be much more active for O_2 reduction than the (111) plane; there is some uncertainty about the (110) plane (ref. 10). Earlier studies on gold have been made on sheets or wires where the gold must have had the fcc cold-worked texture, in which little or no (100) face material is on the surface (ref. 11). On the other hand microcrystallites may present (100) faces at edges.

(2) Microcrystallites of gold may have surface defects which could be active sites, apart from edge effects and orientation effects.

(3) Slightly elevated temperatures, with or without small particles, could have a positive effect on the reduction of oxygen (ref. 12).

The success of the Au-10% Pt electrode may be attributed to factors such as these:

(1) edge effects and surface defects of the particles
(2) avoidance of a support phase; a catalyst that could also be its own current carrying support would in effect suffer no dilution of its activity

Improvement of the oxygen electrodes in the directions of higher temperature operation, high current densities, and long life may well be sought with these factors in mind. Defect mixed oxides of transition elements are plausible candidates (refs. 13 and 14) for research in these directions.

CONCLUSIONS

1. Parameters obtained from cyclic voltammetry are of limited use in predicting fuel cell performance of the cathode. Half-cell polarization measurements offer the closest simulation of the performance of the oxygen electrode, although a predictor of electrode life is still lacking.

2. Micro-particle, micro-crystalline Au, which with 10 wt % Pt is the catalyst of the IFC cell used in Orbiter, accomplishes oxygen reduction by itself. The relatively heavy loading, 20 mg/cm^2, contributes to electronic conductivity.

3. The very low polarization of the Au-10% Pt catalytic electrode suggests that the direction to take for improvement, e.g., in the search for elevated temperature operation and more sinter resistance, should be strongly biased toward unsupported single-phase catalysts.

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TABLE I. - COMPOSITION OF THE ELECTRODES

Specimen number	Description
1	0.5 mg Pt/cm^2 on Vulcan XC 72. This is used as the anode in acid fuel cells, where it may be loaded as low as 0.25 mg/cm^2. The carbon is "Turbostatic Black;" i.e., it has some crystallographic ordering within the basal plane.
2	1.0 mg Pt/cm^2 on acetylene black. This carbon is somewhat more ordered than XC 72, and more resistant to alkali.
3	1.0 mg Pt/cm^2 on previously heat treated (2700 °C) XC 72. The carbon is strongly ordered and is alkali resistant. The surface areas of carbons 1 and 2 are similar, and about half that of 1 (Table II).
4	1.0 mg Pt/cm^2 on XC 72, the composite having been heated at 1050 °C, a treatment reported to have had effects beneficial, but not fully understood, on the activity (ref. 5).
5	0.5 mg Pt/cm^2 on "carbon paper". The latter is a thin fibrous sheet incorporating XC 72 carbon with Teflon upon which a Pt-Teflon mixture is pressed. The teflonated wire screen of the preceding is absent.
6	0.5 mg Au/cm^2 on acetylene black. This Au particle size ranges from ~18 Å to 80 Å with a central tendency of ~45 Å. The structure and the fabrication of the electrodes is the same as that of Pt/C electrodes 1 to 4.
7	20 mg/cm^2 of "unsupported" Au-10% Pt dispersed in Teflon and loaded onto a Au plated Ni screen. This specimen came from a commercial IFC (formerly UTC) alkaline fuel cell cathode. The gold particles range from ~100 Å to several hundred angstroms. The 10 % Pt is not all alloyed (ref. 6).

TABLE II. - DATA FROM CYCLIC VOLTAMMETRY AND HALF-CELL POLARIZATION

Number	Electrode description	Pt area from CV; m^2/g	Double layer width, dl; mA	Voltage, v, in 35 percent KOH at 80 °C, corr. for IR and for loading (norm. to 1 mg/cm^2); v at	
				100 mA/cm^2	200 mA/cm^2
1	Pt/C, 0.5 mg/cm^2 on vulcan XC 72	104	3.0	0.78	0.70
2	Pt/C, 1.0 mg/cm^2 on acet. black	42	0.7	0.57	(<0.3)
3	Pt/C, 1.0 mg/cm^2 on XC 72 prior heated at 2700 °C	49	0.5	0.77	0.70
4	Pt/C, 1.0 mg/cm^2 heated together at 1050 °C	32	1.4	0.71	0.64
5	Pt/C, 0.5 mg/cm^2 "carbon paper" (light Teflon)	75	1.05	0.87	0.85
6	Au/C, 0.5 mg/cm^2 on XC 72	N/A	N/A	0.73	0.67
7	Au-10 % Pt, 20 mg/cm^2, unsupported	N/A	N/A	0.90	0.88

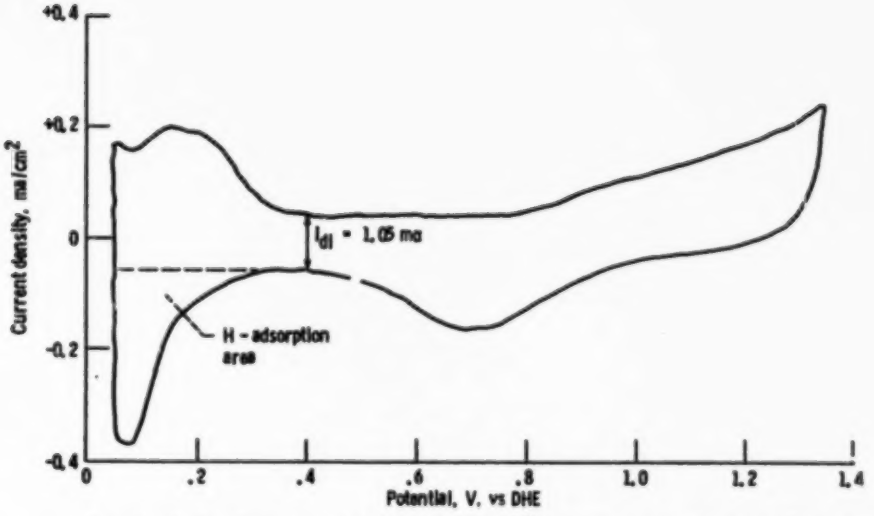

Figure 1. - Cyclic voltammogram of electrode 5, 0.5 mg/cm^2 Pt on carbon paper in H_2SO_4, 25 °C, 5mv/s scan.

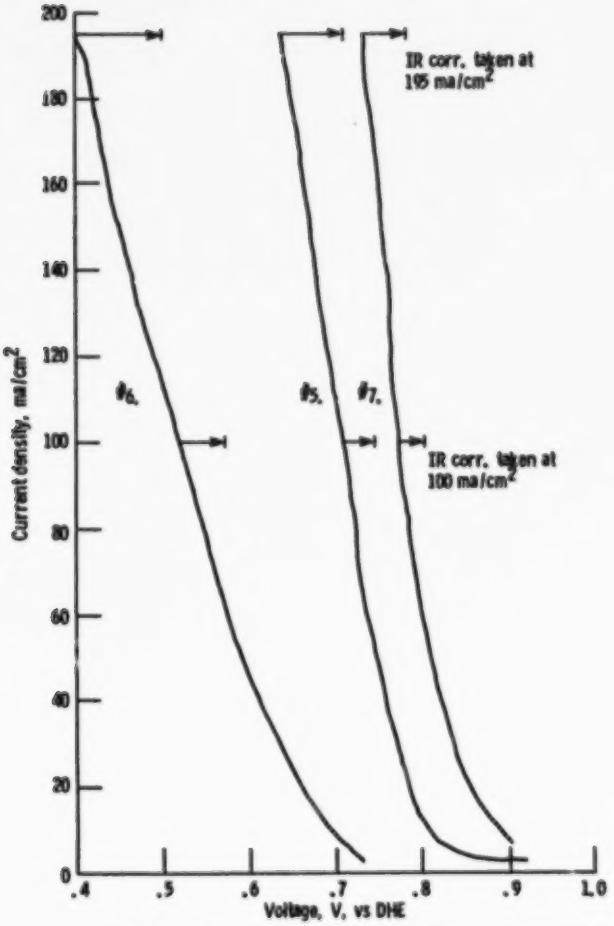

Figure 2. - Floating half-cell current/voltage data from three electrodes. (Tables I and II).

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-87155		

4. Title and Subtitle	5. Report Date
Evaluation Parameters for the Alkaline Fuel Cell Oxygen Electrode	November 1985
	6. Performing Organization Code: 506-41-21

7. Author(s)	8. Performing Organization Report No.
Joseph Singer and Vakula Srinivasan	E-2669
	10. Work Unit No.

9. Performing Organization Name and Address	11. Contract or Grant No.
National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135	13. Type of Report and Period Covered: Technical Memorandum
12. Sponsoring Agency Name and Address	14. Sponsoring Agency Code
National Aeronautics and Space Administration Washington, D.C. 20546	

15. Supplementary Notes

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16. Abstract

Studies were made of Pt- and Au-catalyzed porous electrodes, designed for the cathode of the alkaline H_2/O_2 fuel cell, employing cyclic voltammetry and the floating half-cell method. The purpose was to obtain parameters from the cyclic voltammograms which could predict performance in the fuel cell. It was found that a satisfactory relationship between these two types of measurement could not be established; however, useful observations were made of relative performance of several types of carbon used as "supports" for noble metal ccatalysts and of some Au catalysts. The best half-cell performance with H_2/O_2 in a 35 percent KOH electrolyte at 80 °C was given by unsupported fine particle Au on Teflon; this electrode, developed by UTC (now IFC), is used in the Orbiter fuel cell.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Fuel cell electrodes	Unclassified - unlimited STAR Category 25

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price*
Unclassified	Unclassified		

*For sale by the National Technical Information Service, Springfield, Virginia 22161